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(54) Refrigeration Method and Cooling Agent

(57) The method comprises complete liquefaction of the cooling agent before its cooling is carried out by dissolving in the components of the mixture liquefied at the working pressure those which are in the vapour phase at the working pressure. The cooling agent includes difluorodichloromethane in the amount of 10—50 vol.%, a component having a normal boiling point within the range from —55°C to 85°C in the amount 10—50 vol.%, a component having a normal boiling point within the range from —30°C to 55°C in the amount of 10—50 vol.%, and a component having a normal boiling point within the range from 16°C to 35°C in the amount of 10—75 vol.%. The use in home refrigerators of the cooling agent of the present invention considerably increases maximum specific cold capacity of the refrigeration unit.

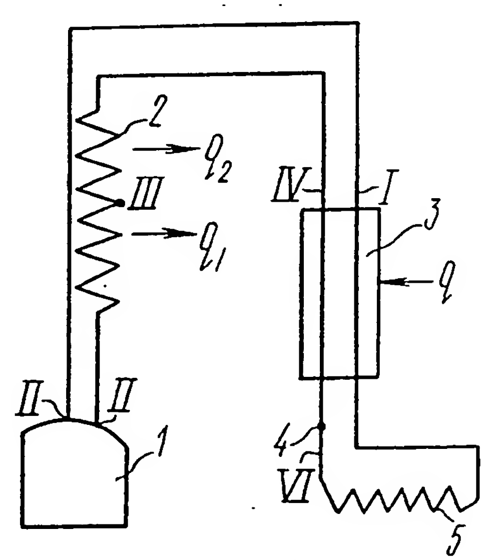

FIG.2

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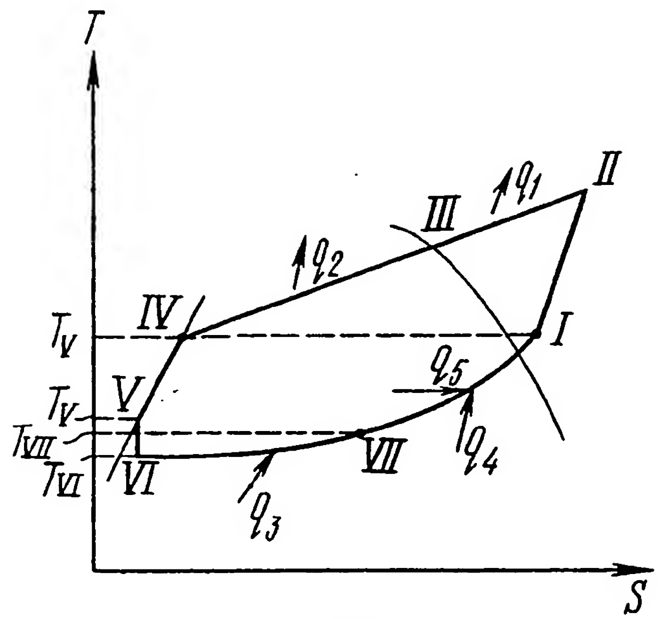
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FIG.1

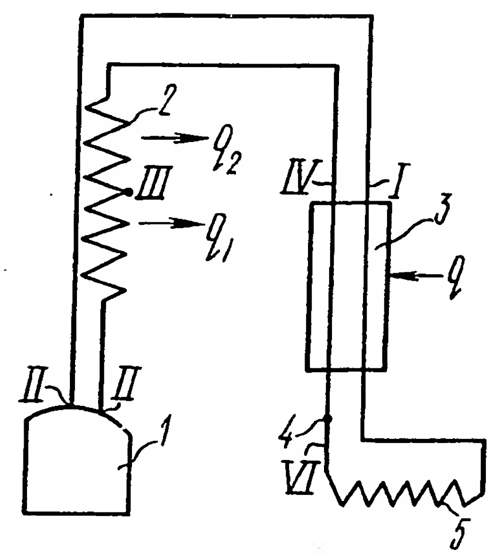
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FIG.2

SPECIFICATION

Refrigeration Method and Cooling Agent

The invention relates to refrigeration methods and to cooling agents for use in such methods, particularly for freezing and storing products.

The method of the invention may be used in the food industry, in the household and in medicine for cooling and freezing, and also in short and long term storage of any products, both food and biological, as well as in other fields of technology wherever it is necessary to obtain and maintain cold at a level of minus 24°C or below at minimum energy requirements.

The invention provides a refrigeration method using a cooling agent comprising a mixture of components boiling at different temperatures and in which the coolant agent is subjected to the following sequence of operations in the following order: compression to a working pressure, partial liquefaction to form a liquid and vapour mixture, complete liquefaction, cooling, throttling, partial and complete evaporation of the cooling agent; complete liquefaction of the cooling agent before its cooling being effected by dissolving in components of the mixture liquefied at the working pressure those among the components which are in the vapour phase at the working pressure.

For effecting complete liquefaction of the cooling agent, the cooling agent is preferably precompressed to a pressure between 10 and 14 kg/cm^2.

In home compression refrigerators having at least two compartments, it is preferred to evaporate the cooling agent partially for providing temperatures enabling freezing and long-term storage in one of the refrigeration compartments, and to evaporate the cooling agent completely for providing temperatures enabling a short-term storage of products, the cooling agent being preferably throttled to a pressure between 0.5 and 3 kg/cm^2.

A cooling agent may be based on difluorodichloromethane containing also at least one component having a normal boiling point within the range from —55°C to —85°C in an amount of between 10 and 50 vol.% such as CO_2 or trifluoromonochloromethane, or trifluoromonobromomethane, a component having a normal boiling point within the range from —30°C to —55°C in an amount of between 10 and 50 vol.% such as difluoromonochloromethane, propane, and at least one component having a normal boiling point within the range from +16°C to —30°C in an amount of between 10 and 75 vol.% such as difluoromonochloroethane, difluoromonochlorobromomethane, octafluorocyclobutane, difluorodichloromethane being used in an amount of between 10 and 50 vol.%.

The cooling agent may contain the components in the following proportioning (in vol.%):

trifluoromonochloromethane	10—50
difluoromonochloromethane	10—15
octafluorocyclobutane	20—70
difluorochloromethane	the balance,
or	
difluorochloromethane	10—15
trifluoromonobromomethane	10—50
octafluorocyclobutane	20—70
difluoromonochloromethane	the balance,
or	
difluorochloromethane	10—15
trifluoromonochloromethane	10—50
difluoromonochloroethane	20—70
difluoromonochoromethane	the balance,
or	
difluorodichloromethane	10—15
trifluoromonochloromethane	10—50
difluoromonochlorobromomethane	10—70
difluoromonochloromethane	the balance,
or	
difluorodichloromethane	10—20
trifluoromonochloromethane	5—30
octafluorocyclobutane	20—60
trifluoromonobromomethane	5—30
difluoromonochloromethane	the balance,
or	
CO_2	10—45
difluorodichloromethane	10—35
difluoromonochloromethane	10—35
difluoromonochloroethane	25—75.

The use of the method and cooling agent for freezing and storing products according to the invention ensures a substantial improvement of the specific cold capacity of refrigeration units in which the method and cooling agent are employed, and also improves cost effectiveness and reliability of such refrigeration units.

Other objects and advantages of the invention will become apparent from the following description of the invention with reference to the accompanying drawings, in which:

Figure 1 shows a cycle of operation of a home compression refrigerator given in the form of a diagram in coordinates temperature v. entropy;

Figure 2 shows a principle diagram of a refrigeration unit for carrying out the method according to the invention.

A method for freezing and storing products in home compression refrigerators consists in loading products into one or several refrigeration compartments in which desired temperature conditions are provided.

A temperature of maximum —24°C for the freezing function and —18°C for the storage function is maintained in the freezing and long-storage compartment. A temperature within the range from 0°C to +5°C is maintained in a short-term storage compartment for all functions of the refrigerator. These temperature conditions are provided owing to the fact that a cooling agent is subjected to the following sequence of operations also illustrated in Figures 1 and 2:

A cooling agent is compressed (process I—II in Figure 1) in a compressor 1 (Figure 2), cooled (process II—III) with the removal of heat (q_1) into the environment, then partially condensed in a condenser 2 for the formation of a liquid and vapour mixture. Non-condensed components of a cooling agent are dissolved in condensed components (process III—IV) with the removal of heat (q_2). Subsequently the cooling agent is fed to a heat exchanger or evaporator 3 where it is cooled to a temperature T_V (process IV—V). The cooling agent is then throttled through a throttle 4 with a temperature decrease from T_V to T_{VI} (process V—VI) and is fed to an evaporator 5 of the freezing and long-term storage compartment with the removal of heat (q_3) from this compartment during long-term storage and from the products in the freezing function (process VI—VII), the cooling agent being heated and evaporated only partially and being in a liquid and vapour phase. Subsequently the cooling agent which is in the liquid and vapour phase is fed to the heat exchanger or evaporator 3 in which the cooling agent is evaporated completely to remove heat (q_4) from the short-term product storage compartment and to remove heat (q_5) from the compressed cooling agent fed to the heat exchanger 3 from the condenser 2.

The cooling agent is then fed to the compressor 1 for re-compression.

The ratio of the pressure of compressed cooling agent (referred to below as cooling agent) to the pressure of expanded cooling agent or a compression ratio P_1/P_2 is substantially lower compared to known methods. Thus, the compression ratio of a refrigeration unit using a widely known method of freezing and storage with the employment of Freon-12 is 14. Optimum value of compression ratio for the method according to the invention is only from 3 to 5. Lower compression ratio results in an improved volumetric efficiency of the compressor which is equal to the ratio of the actual hour capacity of the compressor to the ideal capacity, that is to the volume described by the piston during one hour. Lowering the compression ratio from 14 to 4 results in a 2—3-fold increase in the volumetric efficiency of the compressor, hence in a 2—3-fold improvement of the compressor efficiency and substantial improvement of the efficiency of the refrigeration unit. This brings about a reduction of specific energy consumption for freezing and storing products.

For a complete liquefaction of a cooling agent it is compressed to a pressure between 10 and 14 kg/cm², and to evaporate the cooling agent finally it is enough to throttle it to a pressure between 0.5 and 3 kg/cm².

If a cooling agent is compressed to a pressure below 10 kg/cm² or above 14 kg/cm² and throttled to a pressure below 0.5 kg/cm² or above 3 kg/cm², the process of liquefaction of the cooling agent and its evaporation cannot provide for a desired improvement in the specific cold capacity of the refrigeration unit.

The implementation of the method according to the invention will become apparent from the following embodiment thereof.

A cooling agent in the vapour phase was liquefied in the compressor 1 to a pressure between 10 and 14 kg/cm² and was fed to the condenser 2. The cooling agent was cooled in the condenser 2 to give up heat to the environment (air or water). Owing to the heat removal from the cooling agent vapour, its components boiling at higher temperature where condensed, that is the cooling agent was partially liquefied to form a liquid and vapour mixture, while still being at a higher pressure.

At this pressure and at a temperature between 20 and 45°C a complete liquefaction of the cooling agent was effected by dissolving its components boiling at lower temperature which were in the vapour phase under such conditions, in the liquefied components.

The liquefied cooling agent was cooled in the heat exchangers 3 with a liquid and vapour emulsion, which was formed owing to the partial evaporation of the cooling agent in the evaporator which was fed in the form of a reverse flow to the heat exchanger.

The cooled cooling agent was then fed through the throttle 4 in which its pressure and

temperature were reduced, to the evaporator 5. During the throttling the pressure of the cooling agent was reduced to 0.5—3 kg/cm^2.

The cooling agent boiled (evaporated) in the evaporator 5, a desired amount of heat was removed from objects being cooled so that their temperature decreased as much as to —30°C. This is the process of partial evaporation during which major part of components with lower boiling point are evaporated. After the liquid and vapour mixture have left the evaporator 5, the evaporation of the component with lower boiling point was over, and components of the cooling agent having higher boiling point started evaporating. The process of complete evaporation of the cooling agent was effected in the heat exchanger 3 in which the heat required for the cooling agent boiling was taken off the forward flow as a result of the heat exchange between the forward and reverse flows. The resultant cooling agent vapour was taken off by the compressor 1 for the re-compression thus closing the cycle of operation of the refrigeration unit.

It is preferably to maintain the delivery pressure of 12 kg/cm^2 and the suction pressure of 3 kg/cm^2.

By dissolving non-liquefied components of the cooling agent in its liquefied components in the refrigeration cycle of a single-stage compression refrigeration machine a complete liquefaction of the cooling agent may be achieved at a lower condensation pressure, hence at a lower delivery pressure. This makes it possible to reduce the ratio of the delivery pressure to the suction pressure thus improving the specific cold capacity of the refrigeration unit and the efficiency of the compressor owing to a reduction of energy losses in the compressor.

For carrying out the method according to the invention, it is necessary to choose a cooling agent in such a manner as to ensure desired temperatures for storage and freezing at optimum lowered value of the compression ratio.

For that purpose, a cooling agent contains difluorodichloromethane with a normal boiling temperature of —29.8°C and also components having a normal boiling temperature within the range from —55°C to —85°C, a component having a normal boiling point within the range from —30°C to —55°C, and components having a normal boiling point within the range from +16°C to —30°C.

Such components may comprise any widely known compounds such as CO_2, trifluoromonochloromethane, trifluoromonobromomethane having a normal boiling (sublimation) point of —79.8°C, —81°C, —57°C, —75°C, respectively; difluoromonochloromethane, propane having a normal boiling point of —40.8°C, —40°C, respectively; difluoromonochloroethane, difluoromonochlorobromomethane, octafluorocyclobutane having a normal boiling point of —9.25°C, —3.4°C, —5.8°C, respectively.

Using cooling agents of the following composition minimum cost and maximum effectiveness may be achieved:

1) difluorordichloromethane, trifluoromonochloromethane, difluoromonochloromethane, difluoromonochloroethane;

2) CO_2, difluorodichloromethane, difluoromonochloromethane, difluoromonochloroethane;

3) trifluoromonochloromethane, difluoromonochloromethane, octafluorocyclobutane, difluorodichloromethane;

4) difluorodichloromethane, trifluoromonochloromethane, difluoromonochloroethane, difluoromonochloromethane;

5) difluorodichloromethane, trifluoromonochloromethane, difluoromonochlorobromomethane, difluoromonochloromethane;

6) difluorodichloromethane, trifluoromonochloromethane, octafluorocyclobutane, trifluoromonobromomethane, difluoromonochloromethane; and any other possible combinations.

The components are preferably proportioned as follows (vol.%):

trifluoromonochloromethane	10—50
difluoromonochloromethane	10—15
octafluorocyclobutane	20—70
difluorodichloromethane	the balance;
or	
difluorodichloromethane	10—15
trifluoromonobromomethane	10—50
octafluorocyclobutane	20—70
difluoromonochloromethane	the balance;
or	
difluorodichloromethane	10—15
trifluoromonochloromethane	10—50
difluoromonochloroethane	20—70
difluoromonochloromethane	the balance;
or	
difluorodichloromethane	10—20
trifluoromonochloromethane	5—30

octafluorocyclobutane	20—60
trifluoromonobromomethane	5—30
difluoromonochloromethane	the balance;
or	
CO_2	10—45
difluorodichloromethane	10—35
difluoromonochloromethane	10—35
difluoromonochloroethane	25—75.

If the low-boiling components are used within ranges smaller than those specified above and the high-boiling components are used within ranges greater than those specified above, necessary temperature conditions in refrigerator compartments cannot be provided, that is the temperature in the short-term-storage compartment will be below 0°C and the temperature in the long-term storage compartment will not reach —18°C.

If the low-boiling components are used within ranges greater than those specified above and the high-boiling components are used within ranges smaller than those specified above, the low-boiling components will not be able to dissolve in the high-boiling components, hence desired temperature conditions will not be provided in the short-term storage compartment, that is the temperature in this compartment will be above +5°C.

Each cooling agent is a mixture of components stored in pressurized bottles. A quantity of each component of a volume corresponding to a pre-set percentage of this component in the mixture is discharged from each bottle to a common receiver. First a component having the lowest pressure of liquefied gas vapour, and namely octafluorocyclobutane, difluoromonochloroethane, difluoromonochlorobromomethane, difluorochloromethane is discharged from the bottle to the receiver, then gases with a greater pressure of liquefied gas vapour such as difluoromonochloromethane, trifluoromonobromomethane, trifluoromonochloromethane.

Examples of possible modifications of combinations of components for preparing a cooling agent according to the invention are given below:

Example 1

The following components are mixed: difluorodichloromethane, CO_2, difluoromonochloromethane and difluoromonochloroethane to prepare a cooling agent having the following composition (in vol.%):

difluorodichloromethane	20
CO_2	14
difluoromonochloromethane	20
difluoromonochloroethane	46

When used in home refrigerators, such coolant ensures a compression ratio of between 4 and 5 and provides desired temperature conditions in refrigeration compartments: from 0°C to +5°C in the short-term storage compartment, maximum —24°C in the freezing and long-term storage compartment for the freezing function and —18°C for the long-term storage function.

Example 2

The following components are mixed in a container: difluorodichloromethane, trifluoromonochloromethane, difluoromonochloromethane, octafluorocyclobutane to prepare a coolant having the following composition (vol.%):

difluorodichloromethane	22
trifluoromonochloromethane	10
trifluoromonobromomethane	22
difluoromonochloromethane	22
octafluorocyclobutane	24.

This cooling agent ensures a compression ratio of the compressor between 4 and 5 and maintenance of the following temperature conditions: from 0°C to +5°C in the short-term storage compartment and maximum —24°C in the long-term storage and freezing compartment for the freezing function and —18°C for the long-term storage function.

Example 3

The following components are mixed in a container: difluorodichloromethane, trifluoromonochloromethane, difluoromonochloromethane and difluoromonochloroethane to prepare a cooling agent having the following composition (vol.%):

difluorodichloromethane	25
trifluoromonochloromethane	20
difluoromonochloromethane	25
difluoromonochloroethane	30.

Example 4

A cooling agent having the following composition (vol.%) was prepared by the above-described method:

difluorodichloromethane	10
trifluoromonochloromethane	15
difluoromonochloromethane	25
difluoromonochloroethane	50.

Example 5

A cooling agent having the following composition (vol.%) was prepared by the above-described method:

difluorodichloromethane	20
trifluoromonochloromethane	20
difluoromonochloromethane	10
difluoromonochloroethane	50.

Example 6

A cooling agent having the following composition (vol.%) is prepared by the abovedescribed method:

difluorodichloromethane	20
trifluoromonochloromethane	15
difluoromonochloromethane	25
difluoromonochloroethane	40.

The cooling agents of Examples 3 to 6 ensured the achievement of compression ratio between 4 and 5 and provided in the refrigeration compartments of a compression refrigerator the above-mentioned desired temperature conditions.

In addition to the above-described compositions, the following mixtures can be prepared to provide the desired temperature conditions:

Example 7

difluorodichloromethane	15
trifluoromonobromomethane	50
octafluorocyclobutane	20
difluoromonochloromethane	15.

Example 8

difluorodichloromethane	15
trifluoromonobromomethane	30
octafluorocyclobutane	40
difluoromonochloromethane	15.

Example 9

difluorodichloromethane	10
trifluoromonobromomethane	10
octafluorocyclobutane	70
difluoromonochloromethane	10.

Example 10

difluorodichloromethane	15
trifluoromonochloromethane	50
difluoromonochloroethane	20
difluoromonochloromethane	15.

Example 11

difluorodichloromethane	15
trifluoromonochloromethane	20
difluoromonochloroethane	50
difluoromonochloromethane	15.

Example 12

difluorodichloromethane	10
trichloromonochloromethane	10
difluoromonochloroethane	70
difluoromonochloromethane	10.

Example 13

difluorodichloromethane	15
trifluoromonochloromethane	50
difluoromonochlorobromomethane	20
difluoromonochloromethane	15.

Example 14

difluorodichloromethane	18
trifluoromonochloromethane	20
difluoromonochlorobromomethane	44
difluoromonochloromethane	18.

Example 15

difluorodichloromethane	10
trifluoromonochloromethane	10
difluoromonochlorobromomethane	70
difluoromonochloromethane	10.

Example 16

difluorodichloromethane	15
octafluorocyclobutane	60
difluoromonochloromethane	15
trifluoromonochloromethane	5
trifluoromonobromomethane	5.

Example 17

difluorodichloromethane	29
octafluorocyclobutane	36
difluoromonochloromethane	11
trifluoromonochloromethane	12
trifluoromonobromomethane	12.

Example 18

difluorodichloromethane	10
octafluorocyclobutane	20
difluoromonochloromethane	10
trifluoromonochloromethane	30
trifluoromonobromomethane	30.

The tests showed that maximum specific cold capacity of a refrigeration unit functioning with the cooling agent according to the invention was substantially higher than with the use of prior art cooling agents.

Moreover, the cooling temperature may be lowered by increasing the percentage of components having a boiling point below —50°C at the atmospheric pressure, but this would somewhat lower the specific cold capacity of the refrigeration unit.

The specific cold capacity of the refrigeration unit is substantially improved upon an increase in the content of components having a boiling point above —10°C at the atmospheric pressure, but this results in an increase in the cooling temperature and it may even become close to the boiling point of the highest boiling component of the cooling agent.

Claims

1. A method of refrigeration using a cooling agent in the form of a mixture of components boiling at different temperatures, the method comprising the sequential steps of compressing the cooling agent to a working pressure, partially liquefying the cooling agent to form a liquid and vapour mixture, at least one of the components being in the vapour phase at the working pressure and the other component(s) being in the liquid phase, subsequently completely liquefying the cooling agent by dissolving in the component(s) liquefied at the working pressure the component(s) in the vapour phase at the working pressure, cooling the completely liquefied cooling agent, then throttling it and partially evaporating it, with subsequent complete evaporation of the cooling agent.

2. A method as claimed in claim 1, in which the cooling agent is compressed to a pressure between 10 and 14 kg/cm^2.

3. A method as claimed in claim 1 or 2, in which the cooling agent is partially evaporated so as to obtain temperatures which enable freezing and long term storage of products in one refrigeration compartment of a multicompartment refrigerator, and the cooling agent is completely evaporated by

heating it so as to obtain temperatures which enable short term storage of products in another compartment or compartments of the refrigerator.

4. A method as claimed in any of claims 1 to 3, in which the cooling agent is throttled to a pressure between 0.5 and 3 kg/cm^2.

5. A method as claimed in any of claims 1 to 4, in which the cooling agent contains difluorodichloromethane, at least one component having a normal boiling point within the range from −55°C to −85°C, a component having a normal boiling point within the range from −30°C to −55°C, and at least one component having a normal boiling point within the range from +16°C to −30°C.

6. A cooling agent for carrying out the method as claimed in any of claims 1 to 5, containing, in vol.%:

difluorodichloromethane	10—50
at least one component having a normal boiling point within the range from −55°C to −85°C	10—50
a component having a normal boiling point within the range from −30°C to −55°C	10—50
at least one component having a normal boiling point within the range from +16°C to −30°C	10—75.

7. A cooling agent as claimed in claim 6, the component(s) having a normal boiling point within the range from −55°C to −85°C being selected from CO_2, trifluoromonochloromethane, and trifluoromonobromomethane, the component having a normal boiling point within the range from −30°C to −55°C being difluoromonochloromethane or propane, and the component(s) having a normal boiling point within the range from +16°C to −30°C being selected from difluoromonochloroethane, difluoromonochlorobromomethane, and octafluorocyclobutane.

8. A cooling agent as claimed in claim 7, containing, in vol.%:

trifluoromonochloromethane	10—50
difluoromonochloromethane	10—50
octafluorocyclobutane	20—70
difluorodichloromethane	the balance.

9. A cooling agent as claimed in claim 7, containing, in vol.%:

difluorodichloromethane	10—15
trifluoromonobromomethane	10—50
octafluorocyclobutane	20—70
difluoromonochloromethane	the balance.

10. A cooling agent as claimed in claim 7, containing, in vol.%:

difluorodichloromethane	10—15
trifluoromonochloromethane	10—50
difluoromonochloroethane	20—70
difluoromonochloromethane	the balance.

11. A cooling agent as claimed in claim 7, containing, in vol.%:

difluorodichloromethane	10—15
trifluoromonochloromethane	10—50
difluoromonochlorobromomethane	10—70
difluoromonochloromethane	the balance.

12. A cooling agent as claimed in claim 7, containing, in vol.%:

difluorodichloromethane	10—20
trifluoromonochloromethane	5—30
octafluorocyclobutane	20—60
trifluoromonobromomethane	5—30
difluoromonochloromethane	the balance.

13. A cooling agent as claimed in claim 7, containing, in vol.%:

CO_2 (liquid)	10—45
difluorodichloromethane	10—35
difluoromonochloromethane	10—35
difluoromonochloroethane	25—75.

14. A cooling agent as claimed in claim 13, containing, in vol.%:

CO_2 (liquid)	14
difluorodichloromethane	20
difluoromonochloroethane	46
difluoromonochloromethane	20.

15. A cooling agent as claimed in claim 6, containing, in vol.%:

trifluoromonochloromethane	10
trifluoromonobromomethane	22
difluoromonochloromethane	22
difluorodichloromethane	22
octafluorocyclobutane	24.

16. A cooling agent as claimed in claim 10, containing, in vol.%:

trifluoromonochloromethane	20
difluoromonochloromethane	25
difluorodichloromethane	15
difluoromonochloroethane	40.

17. A method of refrigeration, substantially as hereinabove described with reference to, and as shown in, the accompanying drawings.

18. A cooling agent as claimed in any of claims 6 to 16, substantially as described herein.

19. A cooling agent substantially as described in any of Examples 1 to 18.

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